

MASTER'S THESIS

Voltammetric and spectroscopic studies of dye-immobilised poly(vinyl chloride) membranes

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**Voltammetric and Spectroscopic Studies of
Dye-immobilised Poly(vinyl chloride) Membranes**

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**A thesis submitted in partial fulfillment of the requirements
for the degree of
Master of Philosophy**

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ABSTRACT

A new way of spectroelectrochemical study of dye-immobilised poly(vinyl) chloride (PVC) membrane is proposed. Since there is lack of information on the simultaneous voltammetric and fluorescence response studies, this project can possibly provide important data for the development of a new spectroelectrochemical sensing system. For the first part of the work, an electrochemical cell mounted with a plasticised PVC membrane is specially designed to study the voltammetric response of the PVC membrane upon exposure to various metal. The voltammetric results obtained are comparable to the previous literatures. The electrochemical cell is completely symmetrical so that the coextraction constants of two different metal salts can be simultaneously determined from only one cyclic voltammogram. It is observed that the coextraction constant increases with the lipophilicity of the metal salt and follows with the Hofmeister series of $\text{Li}^+ > \text{Na}^+ > \text{K}^+ > \text{Cs}^+$ and $\text{OAc}^- > \text{Cl}^- > \text{Br}^- > \text{NO}_3^- > \text{ClO}_4^-$ for cations and anions, respectively. The methodology provides a simpler, faster and more convenient way to obtain the coextraction constants of electrolytes compared with the previous techniques.

For the second part of study, a fluorescence dye, fluorescein octadecyl ether octadecyl ester (FODEE), is immobilised in the plasticised PVC membrane. The FODEE-immobilised PVC membrane is mounted on a flow cell which can function as both electrochemical and optical cell. The voltammetric and fluorescence responses of the FODEE-immobilised PVC membrane were simultaneously obtained when it is exposed to various metal salt solutions. The results demonstrate that the fluorescence feature of the

membrane is comparable to that of the voltammetric responses when the membrane is exposed to metal salt solutions and subjected to electric potentials. The fluorescence response can be used to monitor different kinds of ions. It is proposed that the decrease in the fluorescence intensity of FODEE is due to the formation of the FODEE fluorescence inhibited form in the membrane which is determined by the kinds of the extracted ions and polarities of the applied potentials.

The final part of the project is to study the voltammetric and fluorescence responses of an FODEE-immobilised PVC membrane when it is in contact with *n*-alkylammonium ions. It is found that the coextraction constant of *n*-alkylammonium chloride increases as the carbon number in the *n*-alkylammonium ion increases. Furthermore, fluorescence enhancement effect on the FODEE-immobilised PVC membrane is observed as the carbon number in *n*-alkylammonium ion increases. It is proposed that the fluorescence enhancement effect is due to the formation of the FODEE enhancement form in the membrane. Finally, the coextraction constant and fluorescence enhancement effect of the FODEE-immobilised PVC membrane upon exposure to *n*-alkylammonium ions are investigated when the membrane composition is varied. It is found that the percentage of PVC in the membrane can affect the coextraction constants for the *n*-alkylammonium ions and also the fluorescence response of the FODEE-immobilised PVC membrane.

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